

# PATENT SPECIFICATION

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## (54) TREATMENT OF LIGNEOUS MATERIAL

(71) We, BP CHEMICALS LIMITED, of Britannic House, Moor Lane, London, EC2Y 9BU, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process for increasing the digestibility of lignocellulosic materials.

It is known that lignocellulosic materials have a substantial amount of cellulose which is in a combined form with lignin and hence is not digestible by ruminants. The bond between lignin and cellulose in such materials is sufficiently strong to withstand rupture by digestive metabolic process in the rumen. This renders such materials unsuitable and uneconomic as a ruminant feed since the 'available' cellulose is very limited. A considerable amount of work has been carried out to improve the digestibility of straw and other lignocellulosic products. The prior art processes have chiefly used various forms of alkali treatments under severe conditions. One such treatment is claimed and described in GB 1,366,138 (Unilever) which involves intense mechanical working with aqueous alkali. It has also been suggested in the past that the breakdown of the lignin-cellulose bond, especially for the paper making industry, may be facilitated by injecting a special inoculum or culture of lactobacilli into the lignocellulosic material. Whilst such processes improve the 'available' cellulose content of such materials, they are industrial techniques needing considerable skill and sophisticated equipment. Therefore, they do not lend themselves readily to relatively small scale operations, especially on the farm.

It is an object of the present invention not only to use more moderate and natural processes but also to preserve the modified lignocellulosic material thus produced from attack by undesirable bacteria such as the Clostridia species.

Accordingly, the present invention is a process for improving the digestibility of lignocellulosic material comprising mixing the said material with formic acid of a salt thereof

in the presence of water and in the presence of a nutrient capable of sustaining the growth of microorganisms, and storing the mixture under substantially anaerobic conditions.

This is a surprising development since it is known that acids, particularly organic acids, are not sufficient in breaking the lignin-cellulose bond in such materials. We believe the reason for this to be the capability of formic acid in the conditions of a silo to provide the proper environment for the relatively rapid growth of desirable microorganisms in the presence of the nutrient and moisture, which in turn proliferate and attack the lignin-cellulose bond. In addition formic acid acts as a preservative in the product against the growth of undesirable organisms such as the Clostridia species.

The lignocellulosic materials which can be treated under the present invention include straw, green straw, waste paper, sugar cane, bagasse and wood chips.

The nutrient added to the lignocellulosic material being treated facilitates the proliferation of the desirable microorganisms under the conditions of the invention. Suitable examples of nutrients that may be used as additives include, green crops, molasses, sugar cane, silage effluents and milk whey. Some lignocellulosic materials contain sufficient nutrient themselves to sustain the growth of microorganisms and additional nutrient need not be added. For example, if sugar cane is treated in this manner to improve the available cellulose content thereof there will be no need to add a nutrient.

Where a mixture of a nutrient and lignocellulosic material is used, the ratio of these two may vary between 1:99 and 80:20 by weight based on the actual weight of the two.

In order to improve the wettability of the lignocellulosic material and to speed the even spread of the acid, nutrient and water, it may be desirable to add conventional surfactants such as sodium alkyl sulphoethanolamines; ammonium or sodium alkyl arylpolyether sulphonates; alkyl sulphonates; alkyl aryl sulphonates; sulphonated fatty acids; and sodium dialkyl sulphosuccinates.

Moisture content is another factor relevant to the proliferation of the desirable micro-

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organisms. The mixture suitably contains at least 20% by weight of water based on the weight of the lignocellulosic material and preferably between 40 and 70% by weight. As with the nutrient it will be clear that for lignocellulosic material inherently containing the desirable amount of water, such as green straw, water from an external source need not be added.

The amount of formic acid in the mixture is suitably between 0.1 and 5.0 percent, preferably between 0.25 and 0.5 percent based on the fresh weight of the material. The formic acid may be added as a free acid or may be introduced into the mixture as a salt which ionises to the formate ion *'in situ.'*

Suitable examples of salts which may be added to the mixture for this purpose include neutral formates, acid di-formates and acid tetraformates of Group I and/or Group II metal ions or ammonium ions. Ammonium di- and tetra-formates, sodium di- and tetra-formates, calcium tetra-formate and magnesium tetra-formate are preferred.

In addition to formic acid, the acidic component of the additive may contain mineral acids such as hydrochloric acid.

It should be noted that the process of the present invention is distinct from an ensiling process. Ensiling is used for conserving crops which are unstable because they contain a high nutrient and moisture content and hence give rise to mould growth and putrefaction, and provides a means of preservation of existing feed value, which otherwise reduces with time. In contrast to the ensiling process, the present

invention relates to the treatment of relatively stable, dry materials which may contain little or no nutrient (and are hence less susceptible to moulding) in order to increase the feed value of such materials.

The process of the present invention is further illustrated with reference to the following examples.

#### EXAMPLES.

##### Anaerobic Storage Tests.

To obtain the compositions quoted in the following Examples chopped wheat straw was sprayed with a solution of formic acid and nutrient contained in sufficient water to produce a 50% water content in the final mixture. The treated mixture was then stored at 23°C in gas jars fitted with fermentation locks to achieve anaerobic conditions.

After the storage period the dry matter digestibility of the straw was determined by the following procedure:

Samples were dried at 100°C for 18 hours and then ground in a knife mill fitted with a 1mm screen. Buffered cellulase enzyme (*Trichoderma Viride*), 20 ml, was then added to 200 mg of sample weighed into a 25 ml screw-capped bottle, which was then placed in an incubator at 40°C for 48 hours, with shaking twice daily. After incubation the mixture was filtered. The residue was washed well with water and acetone, dried overnight at 100°C and weighed. The percentage digested of the original sample was then calculated.

The following results were obtained:

% Nutrient in Stored Mixture (wet weight basis)	% Formic Acid in Stored Mixture (wet weight basis)	Storage Period (days)	% Dry Matter Digestibility of Straw	% Increase in Digestibility During Storage
None	None	Nil	27.2	None
1 80 green grass	0.5	56	36.4	33.8
2 50 silage effluent	0.5	66	36.5	34.2
3 50 silage effluent	0.5	66	34.6	27.2
4 1.5 molasses				
5 1.5 molasses	0.5	128	34.2	25.7

#### WHAT WE CLAIM IS:—

1. A process for improving the digestibility of lignocellulosic materials comprising mixing the said material with formic acid or a salt thereof in the presence of water and in the presence of a nutrient capable of sustaining the growth of microorganisms, and storing the mixture under substantially anaerobic conditions.
2. A process according to claim 1 wherein the lignocellulosic material is selected from straw, green straw, waste paper, sugar cane, bagasse and wood chips.
3. A process according to claim 1 or 2 wherein the nutrient is selected from green crops, molasses, sugar cane, silage effluents and milk whey.
4. A process according to any of the preceding claims 1 and 2 wherein the nutrient for the mixture is contained in the lignocellulosic material.
5. A process according to any of the preceding claims 1—3 wherein the ratio of nutrient to lignocellulosic material in the mixture is

between 1:99 and 80:20 by weight.

6. A process according to any of the preceding claims wherein the amount of water in the mixture is at least 20% by weight of the lignocellulosic material in the mixture.

7. A process according to claim 6 wherein the amount of water in the mixture is between 40—70% by weight of the lignocellulosic material in the mixture.

8. A process according to any of the preceding claims wherein the water is contained in the lignocellulosic material.

9. A process according to any of the preceding claims wherein the amount of formic acid in the mixture is between 0.1 and 5.0% by weight of the lignocellulosic material.

10. A process according to claim 9 wherein the amount of formic acid in the mixture is between 0.25 and 0.5% by weight of the lignocellulosic material in the mixture.

11. A process according to any of the preceding claims wherein the formic acid is added to the mixture as a salt thereof which ionises to a formate ion 'in situ'.

12. A process according to claim 11 wherein the salt is selected from neutral formate, acid diformate and acid tetra-formate of a Group I or Group II metal ion or an ammonium ion.

5 13. A process according to claim 12 wherein the salt is selected from ammonium di- or tetra-formate, sodium di- or tetra-formate, calcium tetra-formate and magnesium tetra-formate.

10 14. A process according to claim 9 wherein

in addition to formic acid, the mixture contains a mineral acid.

15 15. A process for treating lignocellulosic materials according to any of the preceding claims as hereinbefore described with reference to the Examples.

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